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Section 8d

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June 11, 1993

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Attn: 8(D) HEALTH & SAFETY STUDY REPORTING RULE
(REPORTING)

Dear Sir or Madam:

As required by 40 CFR 716, as amended, rewith submit a copy of the following recently completed health and safety study.

Fate of TDA in Water, Parts I, II, III

Chemical Name	CAS Number
2,4 Toluenediisocyanate	584-84-9
2,6 Toluenediisocyanate	91-08-7
Toluenediisocyaanate (isomer mixture)	26417-62-5

The III reference number 10912, has been marked on the title page of the report. Please refer to this identification number in any communication regarding this study. **The enclosed report does not contain any Confidential Business Information.**

The study is sponsored by the International Isocyanate Institute on behalf of the following:

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BASF Corporation
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Very truly yours,

R. K. Rigger
Managing Director

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FE-E-63

10912

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Summary Report

for

Study on the fate of TDI in water

FE-E-63 Project Parts I, II, and III

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November 17, 1991

Chemical Biotestirg Center

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CONTENTS

1. INTRODUCTION

In FE-E-63 project, we studied the fate of TDI in water under two typical conditions that postulate the accidental release of TDI into aquatic environment. On the basis of the results obtained in FE-E-63 project, the mechanism of the fate of TDI in water was discussed in present report.

2. FEATURES OF THE FATE OF TDI IN WATER

Following features were obtained as to the fate of TDI in water from FE-E-63 studies. (These features were obtained from the experiments carried out at 1000 mg/l of nominal concentration of TDI unless otherwise noted.)

2.1 Disappearance rate of TDI

(1) Vigorous stirring experiment

Under vigorous stirring condition, the disappearance rate of TDI was slowed down with increasing concentration of TDI: From Figure 1 in the report of Part I, the half lives of the disappearance of TDI were about 0.7 and 1.6 hours for 1000 and 10000 mg/l of nominal concentration of TDI, respectively, and they were less than 0.5 hours for 10 and 100 mg/l.

The disappearance rate was also dependent on isomers of TDI: it was about 3 times higher for 2,4-TDI than for 2,6-TDI.

(2) Static experiment

Under static condition, the disappearance rate was significantly dependent on test substance: the half life period of T-0 was slower by a factor of more than fifteen than for T-

100 (they were about 5.2 and 82 days for T-100 and T-0, respectively).

The disappearance rate for T-80 was nearly the same as T-100 for the initial period until about 10 days, but it was slowed down largely after that.

2.2 Kinetics of the disappearance of TDI

(1) Vigorous stirring experiment

The disappearance curves for T-100 (2,4-TDI) and T-0 (2,6-TDI) were interpreted by first-order kinetics:

$$R_t = R_0 e^{-kt}$$

$$\text{or} \quad \ln R_t = \ln R_0 - kt \qquad \text{eq.1}$$

where R_t, k are the residual TDI concentration at time t and first-order rate constant.

Figure 1 shows the logarithm of residual TDI concentration versus time plots for T-100 (2,4-TDI) and T-0 (2,6-TDI) and Figure 2 shows the regression curves to the first-order equation (eq.1) for both test substances.

Table 1 shows the first-order rate constants and the coefficients of determination of the regression analysis. All data were fitted satisfactorily to the curves and the coefficients of determination were high enough to interpret data by the first-order kinetics if a small number of data is taken into account.

On the other hand, data for 2,4-TDI and 2,6-TDI in T-80 were, as the whole, fitted poorly to the first-order kinetics, but if datum at 3 hours or 8 hours was neglected in regression analysis they were fitted satisfactorily to first-order kinetics. Figure 3 shows the regression curves calculated for data until 3 hours and Table 1 shows the first-order rate constants for two isomers in

Table 1 Results of regression analyses by first-order kinetics Data at 8 and 24 hours were ignored in regression analysis for T-80.

Test substance	rate constant (/hour)	Coefficient of determination, r^2
T-100(2,4-TDI)	1.06	0.967
T-80 (2,4-TDI)	0.804	0.995
T-80 (2,6-TDI)	0.760	0.996
T-0 (2,6-TDI)	0.370	0.995

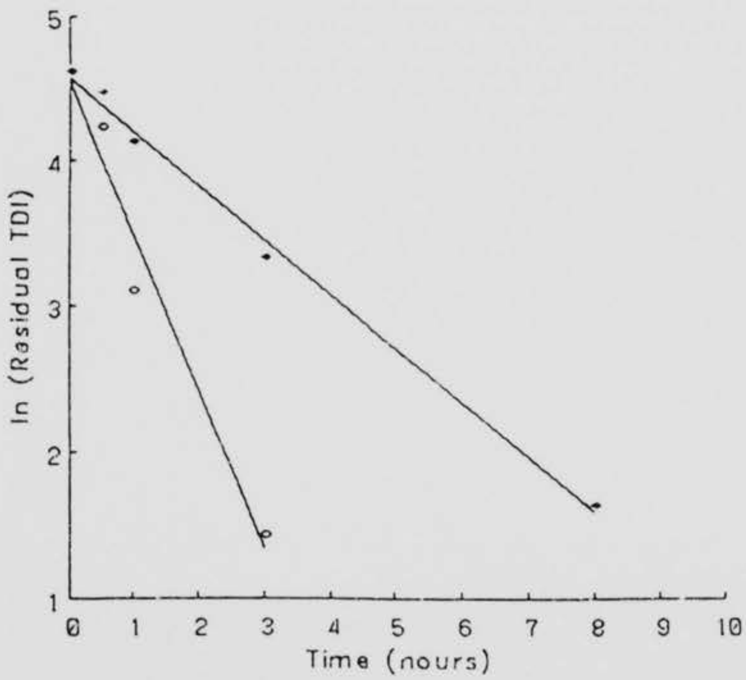


Figure 1 Semi-logarithm plot of percent residues of T-100 (O) and T-0 (●)

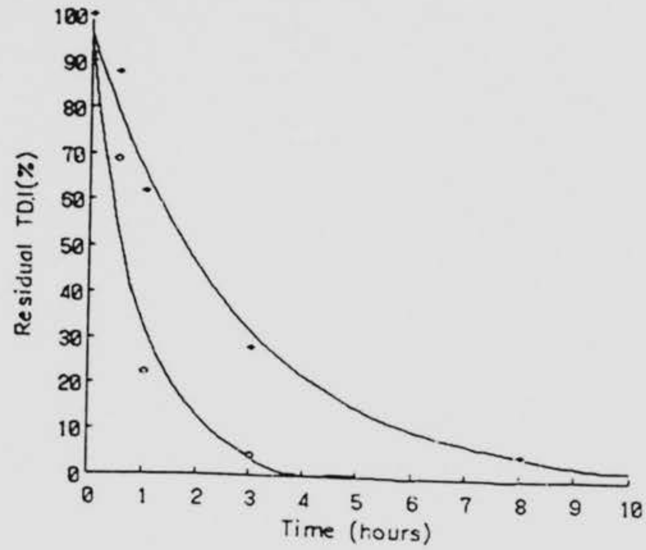


Figure 2 Regression curves for the disappearances of T-100 (O) and T-0 (●)

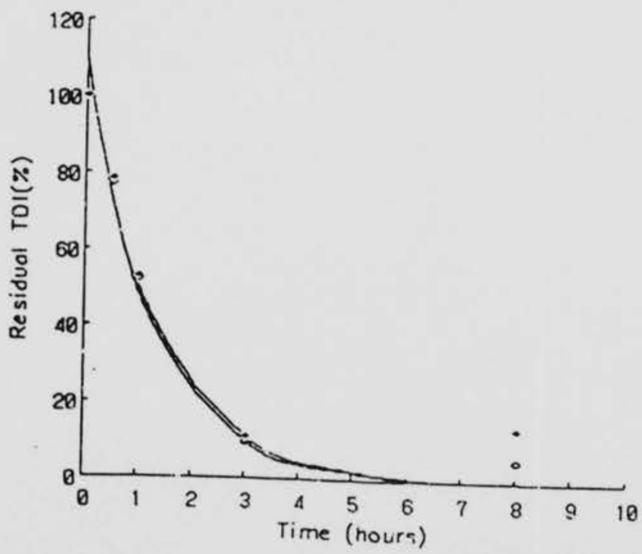


Figure 3 Reg ession curves for the disappearances of 2,6-TDI (●) and 2,4-TDI (O) in T-80

T-80. The rate constants for two isomers in T-80 were approximately consistent within experimental error.

(2) Static experiment

T-0 and T-100 disappeared linearly with time, which indicate that TDI disappeared obeying the zero-order kinetics. The zero-order rate constant of T-0 was smaller by a factor of more than fifteen than for T-100.

On the other hand, the disappearance curve of total T-80 had two phase characteristics, the first phase obeying apparently the first-order kinetics with nearly the same rate as T-100.

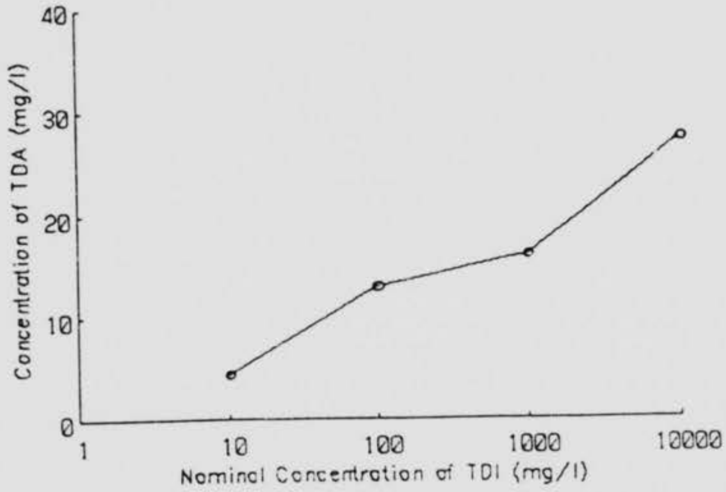
2.3 TDA production

(1) Vigorous stirring experiment

The concentration of TDA increased with time and reached to constant value at the end of test for three test substances. More than 80% of the final amount of TDA were produced within 0.5 hours, at which more than 70% of the substance remained unchanged. Final concentration of TDA increased only by a factor of 6.3 when nominal concentration of TDI was increased 1000 times: they were 4.34 and 27.5 mg/l at 10 and 10000 mg/l of the nominal concentration of TDI, respectively. Molar percent of TDA to total TDA anticipated from the nominal concentration of TDI decreased with increasing the nominal concentration of TDI (Figure 4). Final concentration of TDA in T-0 was about two times higher than that in T-100.

(2) Static experiment

TDA concentration increased with time and reached to the constant values for three test substances. Final concentrations of TDA were about 17, 16.5 and 10 mg/l for T-100, T-80 and T-0, respectively. These values are less than 0.16% of total TDA



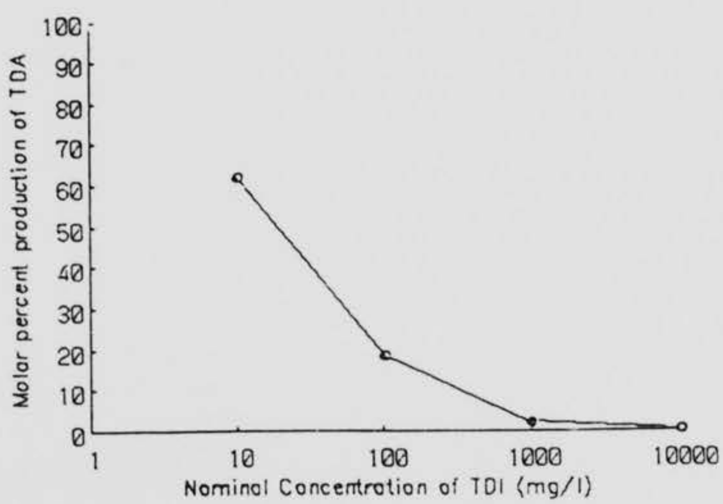


Figure 4 Variation of produced amount (above) and percent production (below) of TDA with nominal concentration of TDI

anticipated from the nominal concentration of TDI.

2.4 Water-soluble reaction product

Total amount of water-soluble reaction product was estimated from dissolved organic carbon (DOC). Under vigorous stirring condition, more than 70% of final DOC was produced within 0.5 hours similarly to TDA for three test substances. The final concentration of DOC became approximately the same values for three test substances.

The percentages of TDA in DOC were 28.2, 32.8 and 59.1% for T-100, T-80 and T-0, respectively.

For T-100, mono-urea and di-urea were identified as water-soluble product and 79% of DOC were comprised of TDA, mono-urea and di-urea.

2.5 Water-insoluble reaction product

The polymerization reaction of water-insoluble product was in progress for T-100 at 8 hours, at which TDI disappeared completely. The number average molecular weight and weight average one of final product were $1.17x10^3$ and $5.58x10^3$, respectively.

3. WHAT KINDS OF REACTION OCCURRED AND WHERE IT PROCEEDED

Before investigating the mechanism of the fate of TDI in water, it must be made clear that what kind of the reaction occur and where it proceed when TDI is put into water.

A series of the reaction occurred in water was initiated by the reaction of isocyanate group in TDI with water to produce the corresponding amine (react.1), which was followed by the reactions between another isocyanate group in TDI and water to produce TDA (react.3') and between amino group and isocyanate one in another TDI to produce oligourea or polyurea compounds (reacts.2 and 4) and so on.

$TDI + H_2O \longrightarrow NCO\text{-}T\text{-}NH_2 + CO_2$	react.1
$TDI + U\text{-}NH_2 \longrightarrow NCO\text{-}T\text{-}NHCONH\text{-}U$	react.2
$U\text{-}NCO + H_2O \longrightarrow U\text{-}NH_2 + CO_2$	react.3'
$NCO\text{-}T\text{-}NH_2 + H_2O \longrightarrow TDA + CO_2$	react.3
$U\text{-}NCO + U\text{-}NH_2 \longrightarrow U\text{-}NHCONH\text{-}U'$	react.4

where T is toluene residue and U is the residue of all reaction products of TDI containing aminotoluene, oligourea and polyurea. TDI disappears through reactions 1 and 2 and then the disappearance rate is given by equation 2 if the rate constants of reaction 2 are the same irrespective of the kind of residue U.

Disappearance rate

$$= k_1(TDI)(H_2O) + k_2(TDI)(U\text{-}NH_2)$$
$$= (TDI)\{k_1(H_2O) + k_2(U\text{-}NH_2)\} \qquad \text{eq.2}$$

where k_1 and k_2 are rate constants of reactions 1 and 2, respectively. On the other hand, TDA and urea are produced through reaction 3' and through reactions 2 and 4, respectively.

Since TDI is scarcely soluble in water (the approximate solubility was estimated in FE-E-93 project), there are two phases of TDI, water and suspended particle phases, which differ in the disappearance rate of TDI because (TDI), (H_2O) and ($U\text{-}NH_2$) in equation 2 are different between two phases. The latter phase is further classified into two phases, the inner phase in suspended particle and interface one between suspended particle and water, from the view point of reaction kinetics between TDI and water because the effective (H_2O) is different between two phases. Accordingly there exist three phases which differ in the disappearance rate of TDI namely water phase, inner phase of suspended particle and interface phase between suspended particle and water. In water phase, (TDI) is very small and (H_2O) is very large, while in inner phase of suspended particle, (TDI) is very large and (H_2O) is very small. Then the disappearance rates of TDI in water and TDI phases are limited by the concentrations of TDI and water, respectively. On the other hand, in the interface phase it is expected that the effective concentrations of water and TDI to participate in the reactions are higher than those in water and inner phases because water and TDI are mixed dynamically in this phase and consequently the disappearance rate of TDI becomes larger compared to both phases.

4. PROPOSED MECHANISM FOR REACTION OF TDI IN WATER

Taking into account the consideration described above, the mechanism of the fate of TDI in water is studied here.
Following two problems must be made clear:

- Which reaction in the reaction 1 to 4 is the rate determining one in the disappearance reaction of TDI in water ?
- In which phase of three phases does it proceed ?

4.1 Vigorous stirring experiment

Proposed mechanism must be able to explain the following features observed in FE-E-63 project:

a. Disappearance reaction of TDI obeyed first-order kinetics.

b. Disappearance rate of TDI slowed down with increasing concentration of TDI.

c. Most of TDA were produced in the period for which most of TDI remained unchanged.

d. Molar percent of TDA to total TDA anticipated from the nominal concentration of TDI decreased with increasing nominal concentration of TDI.

The feature c indicates that the disappearance reaction of TDI and the production one of TDA proceed mostly in separate phase because if these reactions proceed in the same phase, it is thought that the concentration of TDA increases in inverse proportion to one of TDI. Since TDA is produced by successive two reactions of TDI with water, it is difficult to regard the inner phase of suspended particle as the reaction phase of TDA production because in this phase, aminotolueneisocyanate produced by the first reaction with water is easier to react with isocyanate group in another TDI than with water. It is reasonable to expect that TDA is mainly produced in the interface phase because the solubility of TDI in water is small by a factor of about 100 than final concentration of TDA from the result of FE-E-93 project.

During the period for most of TDI to disappear, TDA concentration increased slightly. This observation suggests that the disappearance reaction of TDI proceeded mainly in the inner phase of suspended particle because in this phase, amino group is easily to react with isocyanate one in another molecules and then TDA is difficult to be produced.

Taking into account these consideration, the following reaction mechanism is proposed as the reaction phase and the reaction path for the disappearance of TDI and the production of TDA under vigorous stirring condition.

Proposed mechanism

Reaction proceeded in following two steps:

First step: TDI in interface phase react with water to produce TDA and water-soluble reaction products.

Second step: TDI in inner phase of suspended particle react with water dissolved in the phase to produce mainly water-insoluble reaction products.

The variation of molar percent of TDA production in Figure 4 can be explained by this mechanism as follows: since it is thought that the particle size of suspended particle of TDI in water increase with increasing nominal concentration of TDI, the ratio of interface area to the nominal concentration of TDI decreased and consequently molar percent of TDA production decreased with increasing nominal concentration of TDI because most of TDA are produced by the reaction between TDI in interface phase and water in proposed mechanism.

The result of FE-E-63 project shows that the disappearance reaction of TDI is the first-order one, which indicates that the value of $k_1(H_2O) + k_2(U\text{-}NH_2)$ in eq.2 in the inner phase of suspended particle was constant during whole test period. This condition is satisfied, for example, if reactions 2 and 4 are faster than reactions 1 and 3 and then the concentration $(U\text{-}NH_2)$ was kept to be apparently constant or if the value of $k_1(H_2O)$ was much larger than that of $k_2(U\text{-}NH_2)$ during whole test period because it is considered that the concentration (H_2O) in the inner phase was constant during whole test period.

4.2 Static experiment

The features of the reaction of TDI under static condition are as follows:

a. The disappearance of TDI is zero-order reaction.

b. Similarly to vigorous stirring experiment, the production reaction of TDA in water preceded the disappearance of TDI.

The same considerations as for vigorous stirring condition is valid for static one with regard to the reaction phase and reaction path of TDI disappearance and TDA production and then it is thought that at the first step, TDI in interface phase react with water to produce TDA, followed by the disappearance of TDI in the inner phase of suspended particle of TDI to produce water-soluble reaction product.

Since TDI in the inner phase react with the water which is permeate into the inner phase through the interface between water and TDI phases, two mechanisms for the disappearance reaction of TDI under the static condition, homogeneous and heterogeneous reactions, are supposed: if the permeation rate of water into TDI phase is slower than the reaction rate of TDI with water, the disappearance reaction of TDI proceed heterogeneously from water-TDI interface to the inner of TDI phase parallel to the permeation of water from water phase to TDI phase. Reversely if the permeation rate is faster than the reaction one, the disappearance of TDI and the production of urea bond proceed homogeneously in TDI phase.

In order to determine whether the disappearance reaction of TDI proceed homogeneously or heterogeneously in TDI phase, the following preliminary experiment was carried out: T-80 was placed in glass tube of 8 mm in diameter and 50 cm in length by a height of about 30 cm and water was laid on it by a height of about 10 cm with caution so as not to disturb the interface and the reaction of TDI in TDI layer with water was observed. A[illegible] 24 hours, white reaction product was produced uniformly in TDI layer. This result indicates that the reaction of TDI with water proceed homogeneously in TDI phase. It was also observed in the static experiment of FE-E-63 project that residual TDI was changed uniformly in color from transparence to white even when more than 50% of TDI remained unchanged.

These results support the homogeneous reaction of TDI disappearance in TDI phase under static condition.

If the homogeneous reaction of TDI in TDI phase can be applied to the static experiment, $(TDI)\{k_1(H_2O) + k_2(U\text{-}NH_2)\}$ in eq.2 was constant during whole test period because the disappearance reaction of TDI obeyed to zero-order kinetics. This condition is satisfied, for example, if the value of $k_1(H_2O)$ is much smaller than one of $k_2(U\text{-}NH_2)$ and the concentration $(U\text{-}NH_2)$ is inversely proportional to the concentration (TDI).

In this report, TDI phase was considered as the reaction phase for the disappearance of TDI under both test conditions, but the rate and order of the disappearance reaction under both conditions were different. The difference in the order of the reaction is explained, for example, as follows: under the vigorous stirring condition, since TDI is suspended in small particle, the distance between the inner and interface phases of TDI is shorter and then water molecule in the inner phase is more easily exchanged with one in water phase by Brownian movement than for static condition. Accordingly it is thought that the effective concentration of water in the inner phase under vigorous stirring condition is larger than under static one, which result in the acceleration of the disappearance rate of TDI in the inner phase and in variation of the reaction order. The difference in kinetic patterns of disappearance reaction of TDI under both conditions, however, is difficult to be explained completely only from the data obtained in FE-E-63 project.

The disappearance rate of TDI differed about three times between two isomers in T-0 and T-100, but those of two isomers in T-80 were identical. These results are explained as follows: The rate constants for reactions 1 to 4 are dependent on the chemical structure of the isomer, but the urea formation reactions (reactions 2 and 4) occur not only between the same isomers but also between the different isomers and then the disappearance rates of two isomers in the mixture became identical.

5. EFFECT OF TDI ON AQUATIC ENVIRONMENT

TDI is transformed to various reaction products in water such as TDA, oligourea and polyurea. Of these reaction products, water-soluble one is major species that affect aquatic environment. If the proposed mechanism is applicable to the fate of TDI in natural environment, the majority of water-soluble reaction product is produced by the reaction of TDI in the interface phase with water and then the produced amount of it is proportional to the interface area. From the result of FE-E-63 project, the produced amounts of TDA per cm^2 of the interface area were 1.1, 1.1, 0.67 mg for T-100, T-80 and T-0, respectively.

Provided all TDI in the interface phase is converted to TDA, the thickness of interface phase is estimated from the produced amount of TDA, the interface area and the density of TDI using the following equation:

$$\text{Thickness} = \frac{P \times M}{A \times d \times M'} \qquad \text{eq.3}$$

where P is total amount of TDA produced, A is total area of interface, d is the density of TDI and M and M' are molecular weights of TDI and TDA, respectively.

The thickness of interface phase was 13 um for T-100.

When TDI is spilled into aquatic environment, the amount of TDA produced can be estimated from total area of water-TDI interface and the thickness of interface phase obtained in this study if the assumption hold.

It is observed in FE-E-63 project that 79% of water-soluble reaction product of TDI were composed of TDA, mono-urea and di-urea in T-100. Since these substances are possible compounds to affect the aquatic environment, it is necessary to assess the fate and hazardous effect of these compounds on the environment.

6. Further study for the establishment of mechanism

The following data are required to make clear the mechanism of the fate of TDI in water.

(1) The relationships between the disappearance rate of TDI and the water-TDI interface area and between the amount of TDA produced and the water-TDI interface area.

(2) Molecular weight distribution of water-insoluble reaction product under static condition.

(3) Particle size of the suspended particle of TDI under vigorous stirring condition.

(4) The permeation rate of water into TDI layer if possible.

(5) Identification of water-soluble reaction product other than TDA in vigorous stirring experiment of T-0.

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Attn: 8(D) HEALTH & SAFETY STUDY REPORTING RULE (REPORTING)

Re: Revised Letter of Submission

Dear Sir or Madam:

It has just been noted that there were errors in our submission cover letter to you dated June 11, 1993, the subject of which was the "Fate of TDA in Water, Parts I, II, III". **It should have been entitled, "Fate of TDI in Water, Parts I, II, III".**

Also, the CAS Number for the Toluenediisocyanate (isomer mixture) was incorrectly reported.

Enclosed is a revised letter. Would you please discard the aforementioned letter and replace it with the enclosed.

Thank you for your cooperation.

Very truly yours,

R. K. Rigger
Managing Director

RKR/sha
Enclosure

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(REPORTING)

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The study is sponsored by the International Isocyanate Institute on behalf of the following:

The Dow Chemical Company
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Very truly yours,

R. K. Riggs
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